

BASELINE STUDIES OF PETROLEUM HYDROCARBONS IN CHARLESTON HARBOR

**Final Report to NOAA, Coastal Energy Impact Program
Grant No. CEIP-83-04, October 1984**

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EXECUTIVE SUMMARY

Surface water samples were taken at nine stations in Charleston Harbor on six dates in 1983-84, and analyzed for petroleum hydrocarbons by fluorescence spectroscopy (FS) and gas chromatography (GC). Average hydrocarbon concentrations in three areas of the open harbor ranged from 1.9-5.8 $\mu\text{g/L}$ by FS and 0.8-3.0 $\mu\text{g/L}$ by GC. These are higher than oil residues in the open areas of Winyah Bay, but comparable to levels found in the Sampit River turning basin near Georgetown, SC (1).

Hydrocarbons in both estuaries were heavier than those in No. 2 fuel oil, and had an unresolved complex mixture (UCM) GC hump centered around $\text{C}_{23}\text{-C}_{26}$. Possible sources of these heavy hydrocarbons are: a) discharge of heavy fuel oils and lubricating oils, b) heavy residues of lighter fuels which remain after weathering, c) hydrocarbons from urban runoff and atmospheric deposition.

Some of the factors affecting hydrocarbon analysis by FS were examined. Alumina column chromatography followed by methanolic KOH treatment removed much of the sample fluorescence, with the alumina step providing most of the cleanup. Good sample cleanup is thus essential for accurate FS analysis of oil residues. Hydrocarbon concentrations measured by FS and GC were compared for 50 samples from Charleston Harbor and Winyah Bay. Although the correlation between the two methods was significant, the data showed much scatter. In the 0.5-10 $\mu\text{g/L}$ range, the agreement between an individual GC and FS measurement was a factor of 5-6 at the 95% confidence level.

INTRODUCTION

Increasing development along the coast as well as the possibility of offshore drilling in the future has created a need for baseline measurements of petroleum and other pollutants in South Carolina estuaries. Such data are sparse, especially for organic compounds, and in 1981 we began a study of petroleum residues in the surface water of Winyah Bay, Georgetown, SC (1). The investigation was prompted by a proposal to build a refinery on the Sampit River in Georgetown, and no information was available on hydrocarbon levels in the bay.

Samples were collected on 10 dates in 1981-82 from the Sampit River and Winyah Bay and analyzed for hydrocarbons by fluorescence spectroscopy (FS) and gas chromatography (GC). Oil residues measured by FS as South Louisiana crude (SLC) equivalents averaged 3.3 $\mu\text{g/L}$ in the industrialized portion of the Sampit River, 0.8 $\mu\text{g/L}$ in the upper Sampit River, and 0.5 $\mu\text{g/L}$ in Winyah Bay. These levels are on the low end of the scale for petroleum pollution in coastal waters (1).

Following the Winyah Bay study, we decided to survey Charleston Harbor, a much more heavily industrialized estuary. The objectives were to compare petroleum levels in the two estuaries and to continue a comparison of FS and GC analytical methods, begun in the earlier investigation (1).

EXPERIMENTAL

Study Area and Collection Methods

Charleston Harbor is formed by the junction of the Wando, Cooper, and Ashley Rivers (Fig. 1). Hydrocarbons can enter the harbor via a large number of sources, including: recreational and commercial boat traffic, marinas, industrial discharge, fuel storage facilities, urban runoff from the city of Charleston and atmospheric

deposition. Since the purpose of this project was to measure baseline hydrocarbon levels, we did not try to identify the contributions from various sources. Instead, we measured levels of contamination in surface water of the open harbor.

Collections were made within the top meter of the water column at the nine stations described in Table 1 and shown in Fig. 1 by holding a 3.8-L glass jug under the surface. This was done from the bow while the boat was moving slowly forward to minimize oil contamination from the engine. Bottles used for this work had PTFE-lined caps, and previously contained chromatographic-grade solvents.

Analytical Methods

Procedures for extraction, cleanup, and analysis by FS and GC have been detailed in our previous report (1), and will only be summarized here. The unfiltered samples were extracted with dichloromethane, and the solvent was reduced to 2-3 mL in the presence of hexane. Extracts were cleaned up by alumina column chromatography followed by saponification with methanolic KOH. After adding water, the hydrocarbons were partitioned into petroleum ether and finally diluted to 20 mL with 30% dichloromethane-petroleum ether for FS analysis.

FS work was done in 1-cm silica cells using a Perkin-Elmer MP-43A spectrofluorimeter. Quantitative measurements were made against two API reference oil standards, South Louisiana crude (SLC) and No. 2 fuel oil (No. 2). Excitation (EX) and emission (EM) wavelengths (5-nm bandpasses) were: SLC: 320 nm EX, 380 nm EM; No. 2: 280 nm EX, 325 nm EM.

GC analysis was done after blowing the sample down to ≈ 40 -100 μ L with nitrogen and adding an internal standard (n -C₁₄ or n -C₁₆). Analyses were carried out on a 0.3 cm i.d. x 180 cm long column packed with 3% Dexsil 300 using the program: inject at 80° C, hold 5 min, increase at 8°/min to 260-280°C, hold 15-20 min.

Table 1. Sampling Locations in Charleston Harbor

<u>Station</u>	<u>Description</u>
1	Cooper River, near Westvaco Paper Co.
2	Cooper River, Clouter Creek Reach, near naval shipyard
3	Wando River, near container port
4	Down harbor from Custom House Reach
5	Adger's Wharf
6	South of the Battery
7	Ashley River, marina
8	Fort Johnson, mid-channel
9	Fort Johnson, outside boat slip

Injector and detector temperatures were 220° and 280°. The total chromatogram area for components eluting at or beyond the retention time of n-C₁₂ was calculated by electronic integration. Response factors were derived from a series of n-alkanes in the C₁₂-C₂₄ range.

Most samples were analyzed "whole", although a few were fractionated to better observe the n-alkane distribution. Separations were done on a 3-g silicic acid column (deactivated by adding 5% water) overlain with 2 g neutral alumina (6% water added). Fraction 1 (f₁) containing alkanes and most of the unresolved complex mixture (UCM) was eluted with 25 mL petroleum ether. Fraction 2 (f₂) containing the PAH was eluted with 20 mL 30% dichloromethane-petroleum ether. Further details of the column separation procedure are given in (2).

RESULTS AND DISCUSSION

Analytical Recovery and Precision

Known quantities of oils (SLC and No.2) or individual n-alkanes were added to 3.5 L estuarine water and carried through the analytical procedure. Recoveries of SLC and No. 2, assayed by FS, were about 80% (Table 2). Individual n-alkanes were determined by GC. Losses of C₁₄ and lighter alkanes were observed, probably because of evaporation during the blow-down step, but C₁₆-C₂₄ hydrocarbons were completely recovered (Table 2). The overall precision of the extraction, cleanup, and FS analysis (combined SLC and No. 2 sets in Table 2) was 10%, and 13% for GC analysis (C₁₆-C₂₄ alkanes).

Figure 1

Sampling locations in Charleston Harbor.

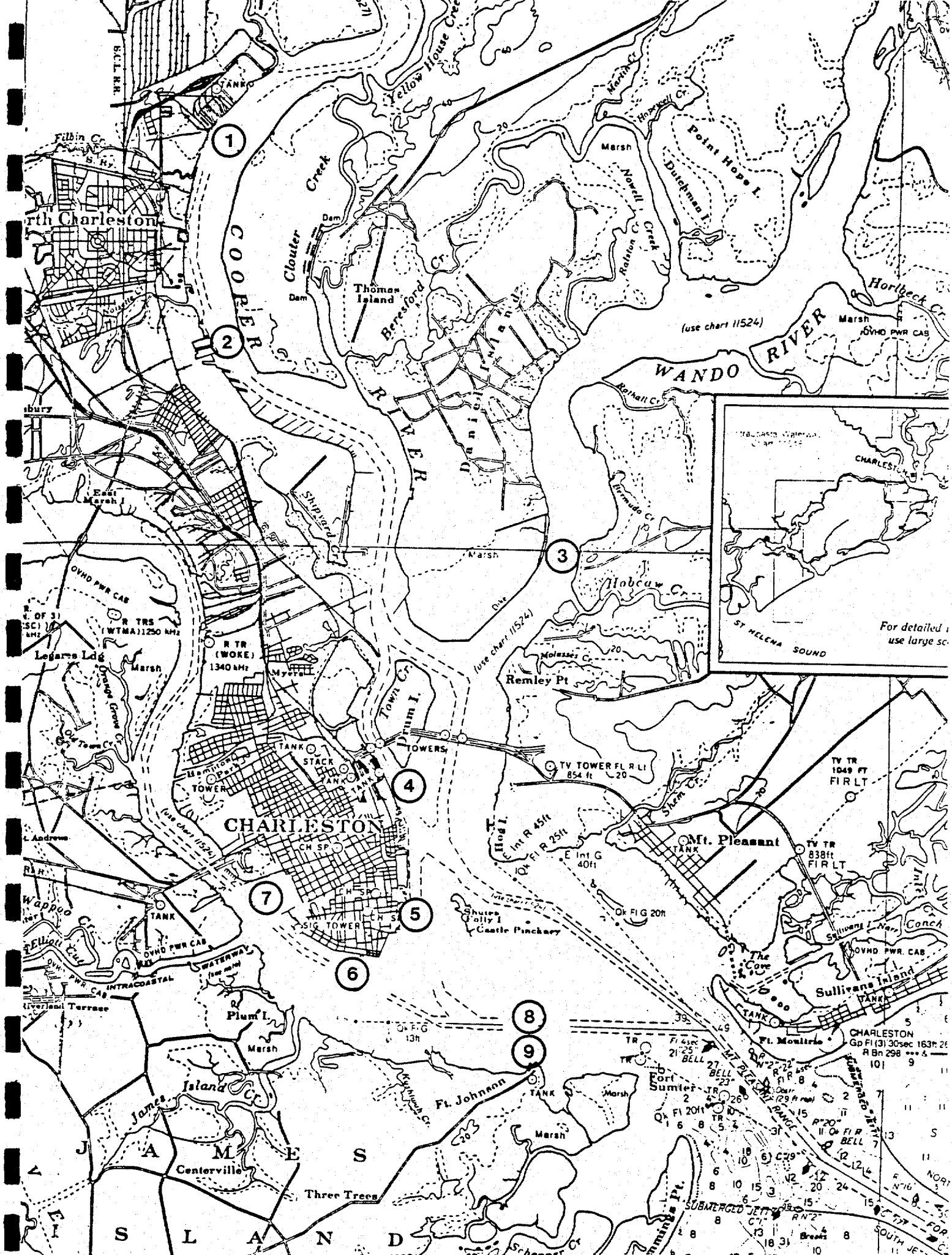


Table 2. Recovery of Hydrocarbons from Spiked Estuarine Water Samples^a

<u>Hydrocarbon</u>	<u>Concentration</u> <u>µg/L</u>	<u>Analytical</u> <u>Method</u>	<u>% Recovery</u> <u>± S.D.</u>	<u>Experiments</u>
SLC	40-200	FS	81 ± 3	4
SLC	9-20	FS	78 ± 12	8
No. 2	25	FS	83 ± 1	2
n-alkanes:				
C ₁₂	0.7	GC	71	1
C ₁₄	0.9-1.1	GC	54 ± 28	3
C ₁₆ -C ₂₄	0.7-1.1 ^b	GC	100 ± 13	4

^a 3.5 liters

^b concentrations of individual alkanes

Effect of Sample Cleanup on FS Analysis

In the Winyah Bay study (1) we found that a large part of the sample extract fluorescence was removed by alumina column chromatography, and was reduced further by saponification with methanolic KOH. SLC was 90% recovered in the saponification step alone, and overall recoveries of SLC and No. 2 from spiked water samples were about 80% (Table 2). Fluorescence losses during sample cleanup were thus due to removal of non-petroleum materials.

We also measured the fluorescence of some Charleston Harbor samples before and after saponification (samples received alumina cleanup), and the results are plotted with the Winyah Bay data in Fig. 2. The regression equation for this plot is:

$$HC = 0.82 HC_s + 0.61 \quad (r^2 = 0.87, n = 74) \quad (\text{Equation 1})$$

where HC and HC_s are FS-determined hydrocarbons ($\mu\text{g/L}$) before and after saponification. The positive intercept in Equation 1 ($0.61 \mu\text{g/L}$) represents fluorescing material that is not petroleum and survives the alumina cleanup procedure. The combination of alumina chromatography and KOH treatment provides the vigorous cleanup needed to accurately measure low oil levels by FS. Whether saponification alone will do the job is a point that we did not examine, but would be worth pursuing.

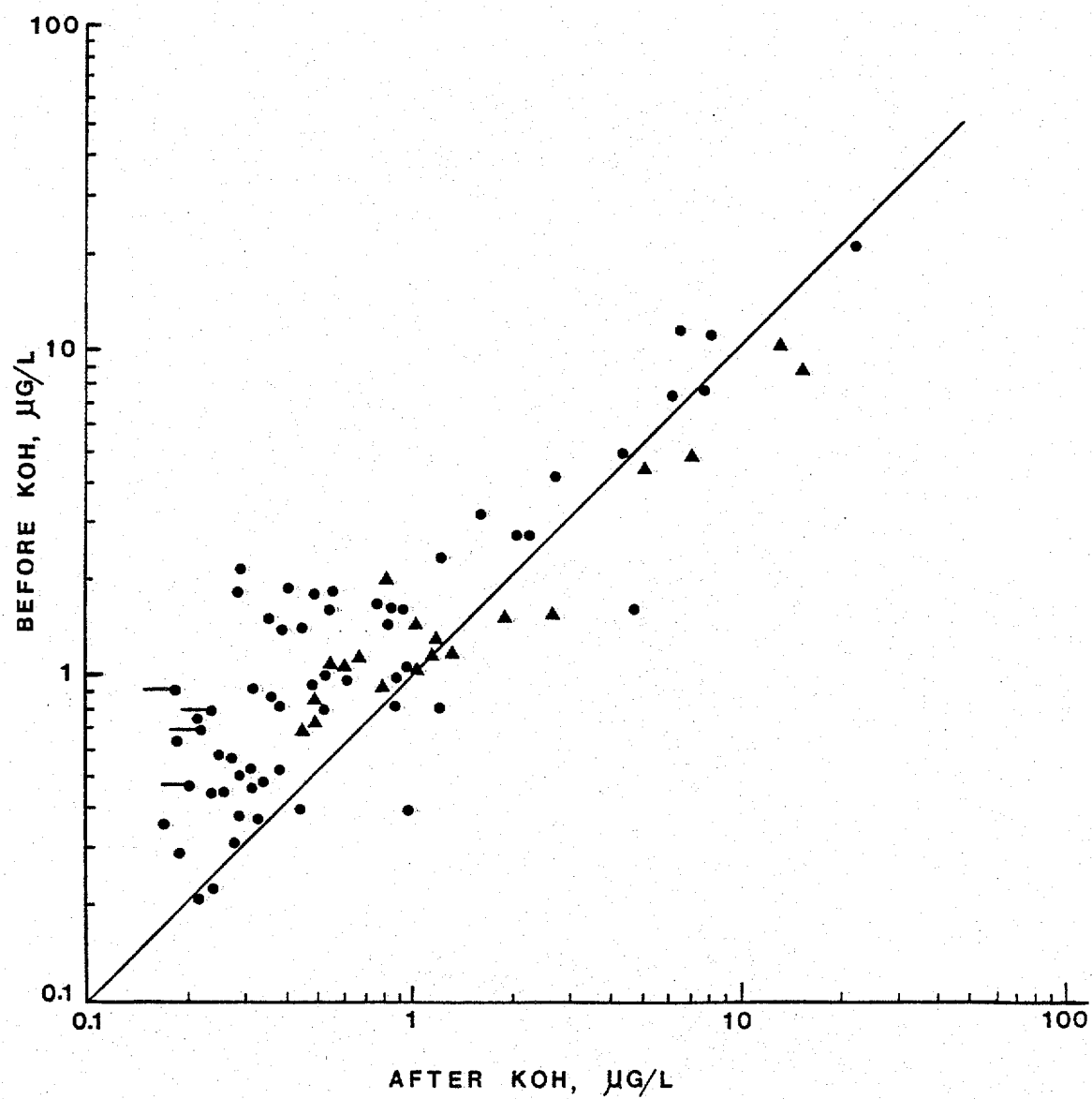
Fluorescence Characteristics of Charleston Harbor Samples

Fluorescence spectra of various oil types have been discussed in our previous report (1). Polycyclic aromatic hydrocarbons (PAH) in oils range from 2-ring compounds (naphthalenes and methylnaphthalenes) to higher molecular weight

Figure 2

Sample fluorescence before and after saponification with methanolic KOH. Extracts were previously cleaned up on an alumina column.

- Winyah Bay
- ▲ Charleston Harbor
- below detection limit after saponification



compounds containing 5 or more rings (e.g. benzopyrenes). The heavier oils contain greater proportions of the high molecular weight PAH and fluoresce at longer wavelengths. Spectra are usually obtained by holding the EX wavelength constant and scanning the EM monochromator (conventional mode), or by scanning both EX and EM monochromators simultaneously with a constant wavelength offset ($\Delta \lambda \sim 10\text{-}20\text{ nm}$) (synchronous mode). Synchronous fluorescence provides more spectral detail and gives more information about the aromatic content of the sample.

Synchronous spectra of Charleston Harbor samples from Feb, 1983 and April, 1983 are compared with some oil spectra in Figs. 3 and 4. The Charleston Harbor spectra are similar to those of Winyah Bay samples (1), and show features of both light and heavy oils. Particularly interesting is the large peak in the samples at 440-450 nm. This peak occurs at the same wavelength as a prominent "bump" in Venezuelan Bunker C (VBC = No. 6 fuel oil), and suggests the presence of heavy PAH, possibly residues from oil weathering or combustion PAH from aerial fallout. An alternative explanation is the PAH perylene, which is formed naturally in reducing sediments and has a strong synchronous doublet in the 440-460 EM nm region (3).

Quantitative Measurements by FS

Petroleum concentrations were measured as SLC or No. 2 equivalents by using these oils as fluorescence standards. Measurements against each reference oil were made at different wavelengths, as explained in the Analytical Methods section. However because of spectral overlap, the SLC and No. 2 equivalents should not be added to give total oil.

Oil concentrations at each station are given in Table 3. In most cases the results based on No. 2 were about the same or lower than those calculated as SLC. If

Table 3. Hydrocarbons in Charleston Harbor Surface Water Measured by FS, $\mu\text{g/L}$

Collection Date

Station	Oil Standard ^a	6/2/82	2/19/83	4/30/83	6/84	2/16/84	3/2/84
1	SLC No. 2		0.82	1.3 0.95	1.2 0.66	3.1 2.9	1.7 0.68
2	SLC No. 2		0.49	2.7 3.7	2.7 1.4	5.3 5.2	2.1 1.8
3	SLC		0.49				
4	SLC No. 2		0.45	1.2 1.5	2.6 1.3	24.5 14.0	2.5 2.3
5	SLC	7.2					
6	SLC No. 2		1.0	0.86 1.2	3.4 1.0	18.3 8.8	3.0 0.94
7	SLC No. 2			5.3 2.9	7.0 1.8	10.8 6.9	4.2 1.7
8	SLC No. 2		0.62	1.1 1.5	2.1 1.1	4.5 2.3	1.3 0.83
9	SLC	13.4					

a) SLC = South Louisiana crude oil, EX = 320, EM = 380 nm
 No. 2 = No. 2 fuel oil, EX = 280, EM = 325 nm

Figure 3

Synchronous fluorescence spectra (5 nm bandpasses) of two Charleston Harbor samples from Feb. 1983 and some oil standards (No.6, No. 2, and SLC). EX and EM wavelengths in nm are given on the abscissa.

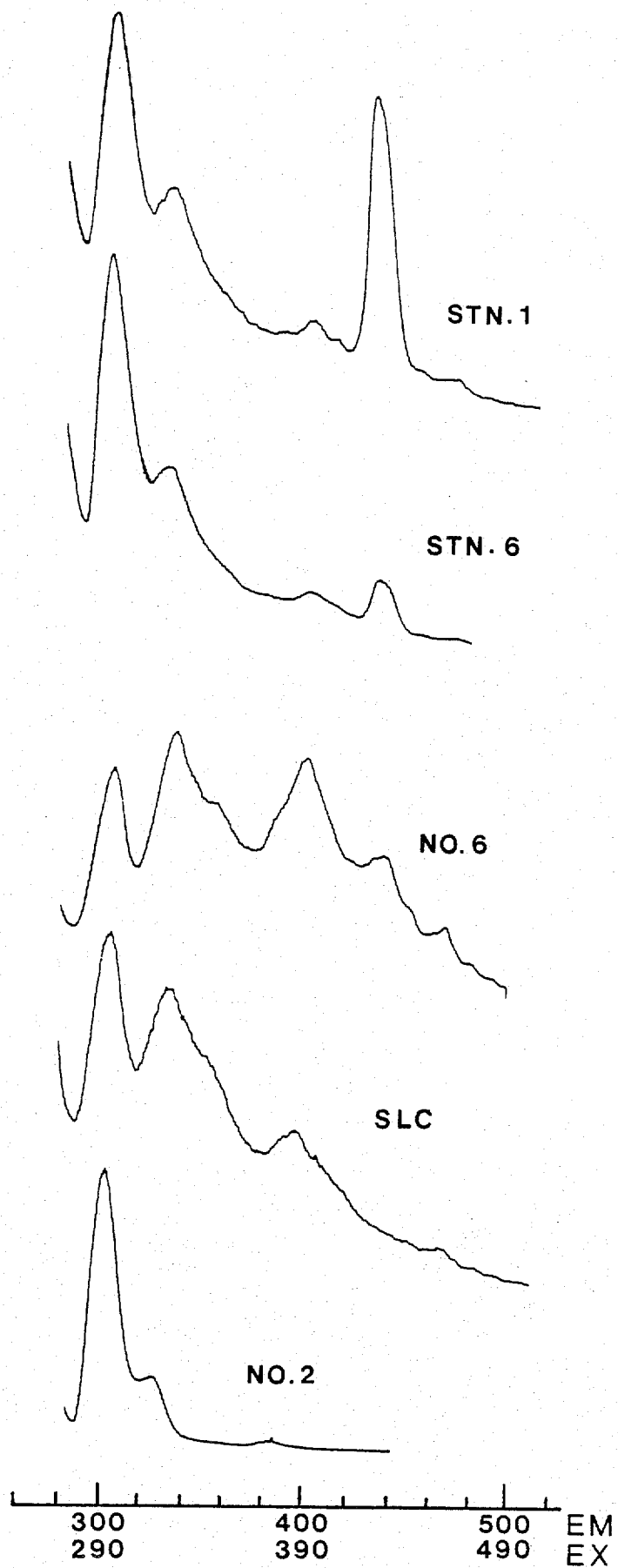
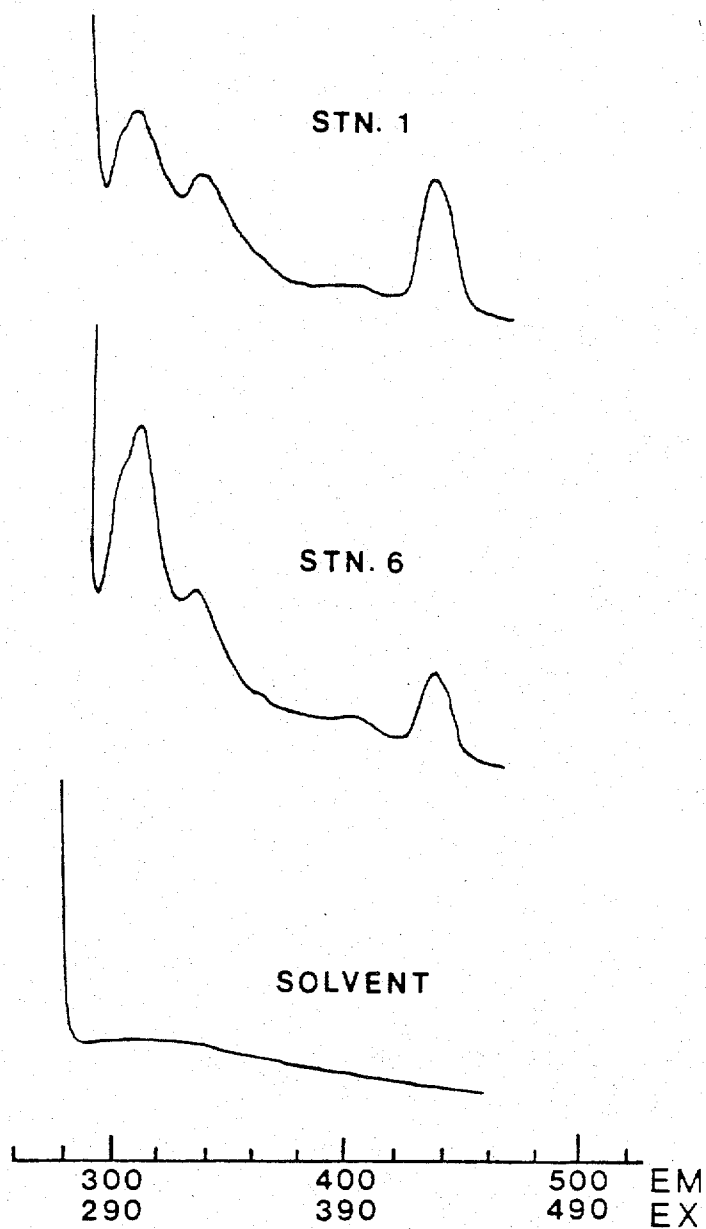


Figure 4

Synchronous fluorescence spectra of two Charleston Harbor samples
from April 1983



oil residues in the harbor were mainly light diesel fuel, the No. 2 equivalents would be higher. Both the spectra (Figs. 3 and 4) and quantitative FS data indicate a greater proportion of the heavier PAH in harbor water than present in No. 2, and gas chromatograms also show a heavy hydrocarbon pattern (see next section).

On four dates duplicate samples were collected at several stations, and on one occasion four samples were taken at a single station (Table 4). At times duplicates agreed very well, but in many cases a two-fold or more difference was observed for samples taken within a few minutes of each other. The same situation was encountered in the Winyah Bay work (1). Since the overall analytical precision is $\pm 10\%$ (Table 2), these differences cannot be accounted for by the analytical procedure. We think the results in Table 4 reflect real differences in sampling the water column, possibly because of variation in oil concentrations within the water or different amounts of slick material pulled into the bottles when they pass through the surface.

GC Analysis of Hydrocarbons

Chromatograms of Charleston Harbor samples showed a series of resolved peaks, often on top of a UCM (Figs. 5-7). Most of the UCM eluted in f_1 , and was centered around C_{23} - C_{26} (Figs. 8 and 9). This hydrocarbon distribution was similar to that in Winyah Bay samples (1), although oil concentrations in Charleston Harbor were generally higher. The C_{14} and lower alkanes were partially lost in our analytical procedure so samples would have shown reduced amounts of these components, if present. However, most of the organic material in water extracts eluted after C_{20} , with only small amounts in the C_{16} - C_{20} region. Since these alkanes were completely recovered during analysis, Figs. 5-9 give an unbiased picture of the heavy hydrocarbon proportions in surface water.

Table 4. Replicate Collection and FS Analysis of Hydrocarbons in Charleston Harbor

Oil Equivalents, $\mu\text{g/L}$ (Individual Samples)

<u>Date</u>	<u>Station</u>	<u>SLC</u>	<u>No. 2</u>
6/2/82	9	13, 15	
4/30/83	1	0.81, 1.9	
	6	0.63, 0.60, 0.99, 1.3	
2/16/84	1	2.3, 3.4	3.1, 2.7
	2	7.3, 3.2	6.9, 3.4
	4	10, 39	7.7, 20
	6	15, 22	8.6, 9.0
	8	2.3, 6.6	2.1, 2.4
3/2/84	1	1.6, 1.8	0.68, 0.68
	2	2.1, 2.6	1.8, 3.0
	4	2.2, 2.6	0.58, 3.2
	8	1.2, 1.3	0.6, 1.1

Figure 5

Chromatograms of Charleston Harbor samples from Feb. 1983.

Numbers on abscissa mark elution positions of n-alkanes. Starred peaks (*) are analytical artifacts. Injection volumes were 8-9 μL out of 80-90 μL total volume. IS = internal standard.

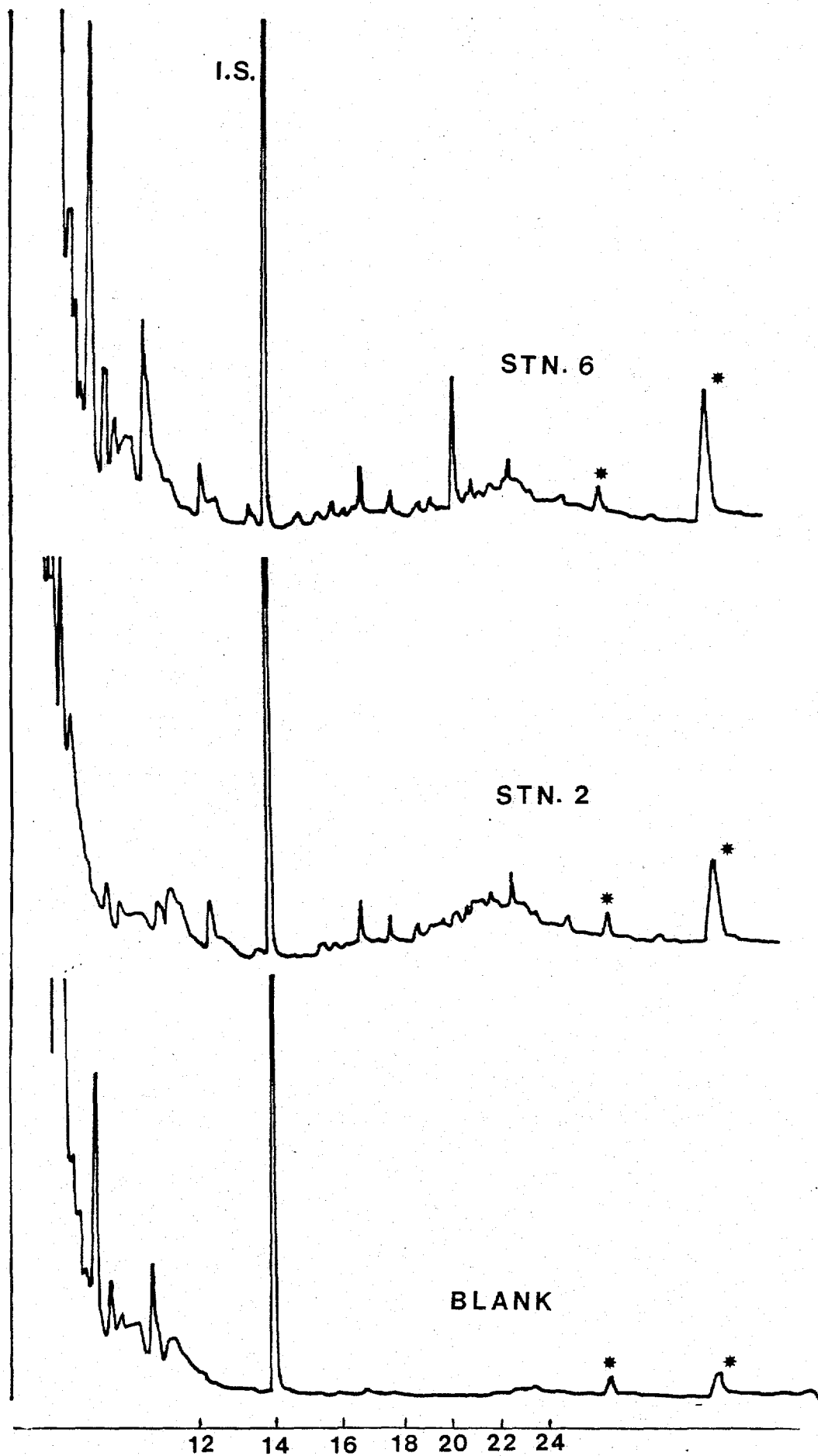


Figure 6

Chromatograms of Charleston Harbor samples from March 1984,
8-10 μL injected out of 80-100 μL total volume. See Fig. 5 for symbols
explanations.

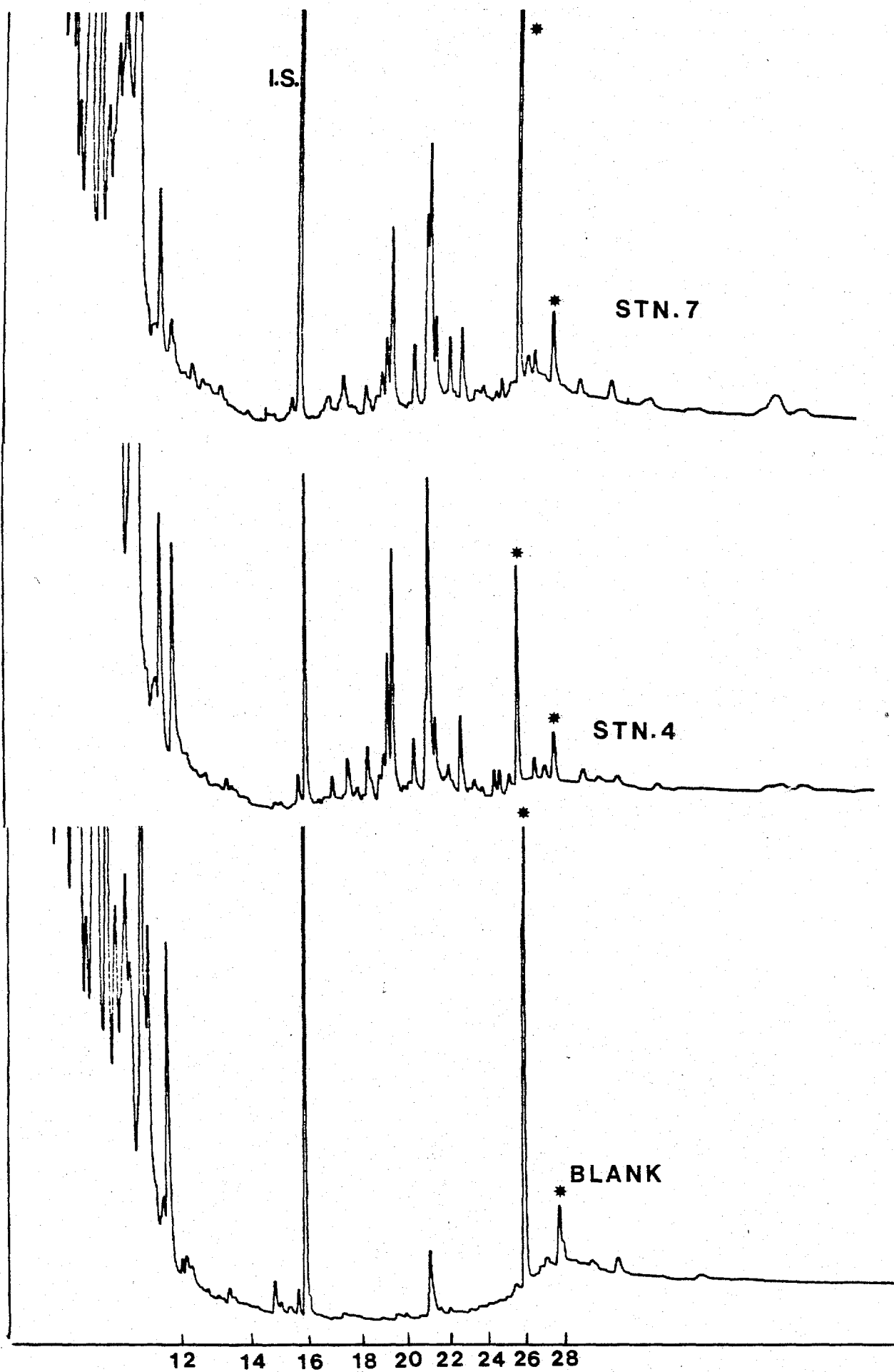


Figure 7

Chromatograms of Charleston Harbor samples from Feb. 1984, 7-9 μL injection out of 60-100 μL total volume. See Fig. 5 for symbols explanations.

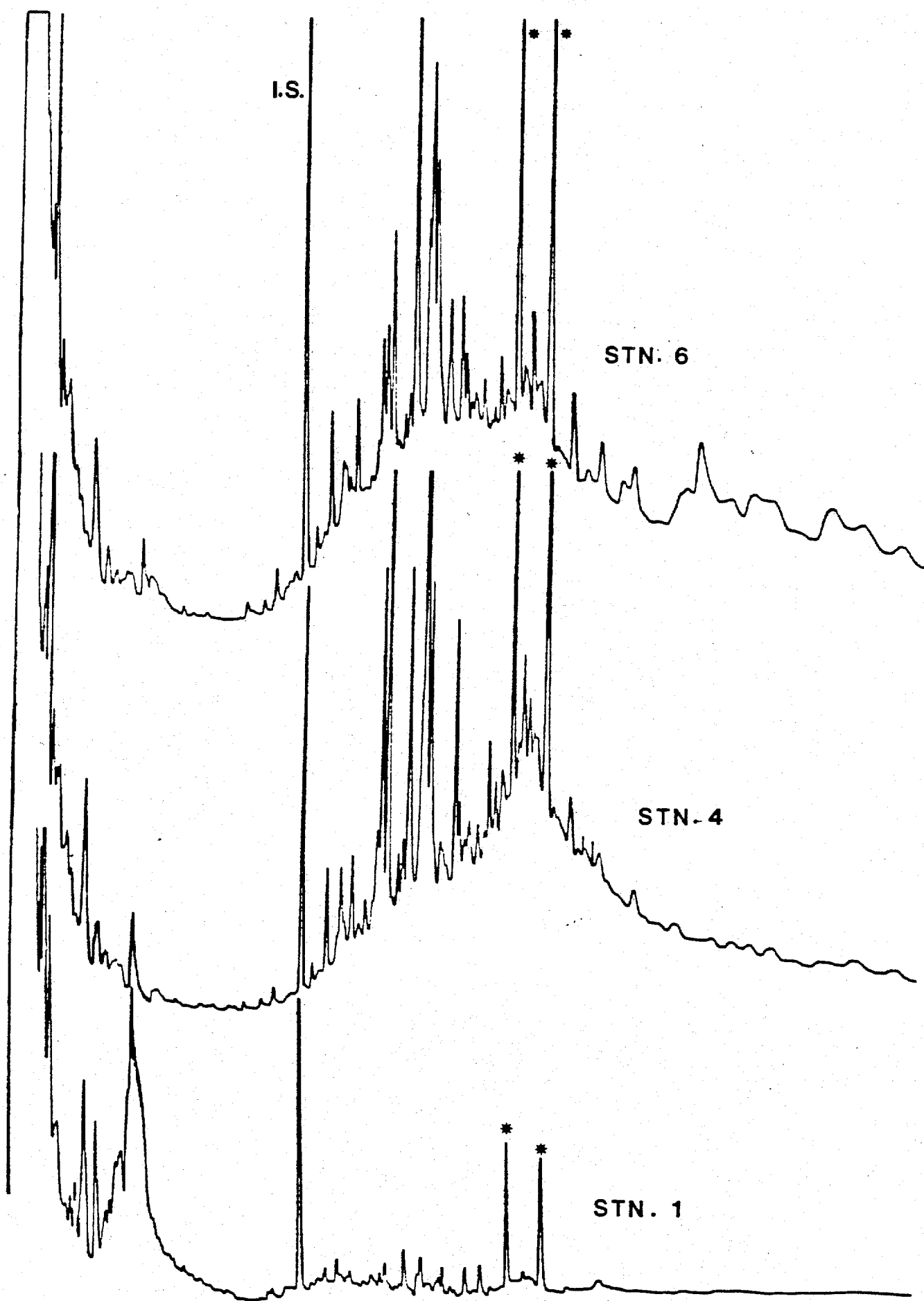


Figure 8

Chromatograms of f_1 and f_2 hydrocarbons from Station 4, Feb. 1984.

See Fig. 5 for symbols explanations.

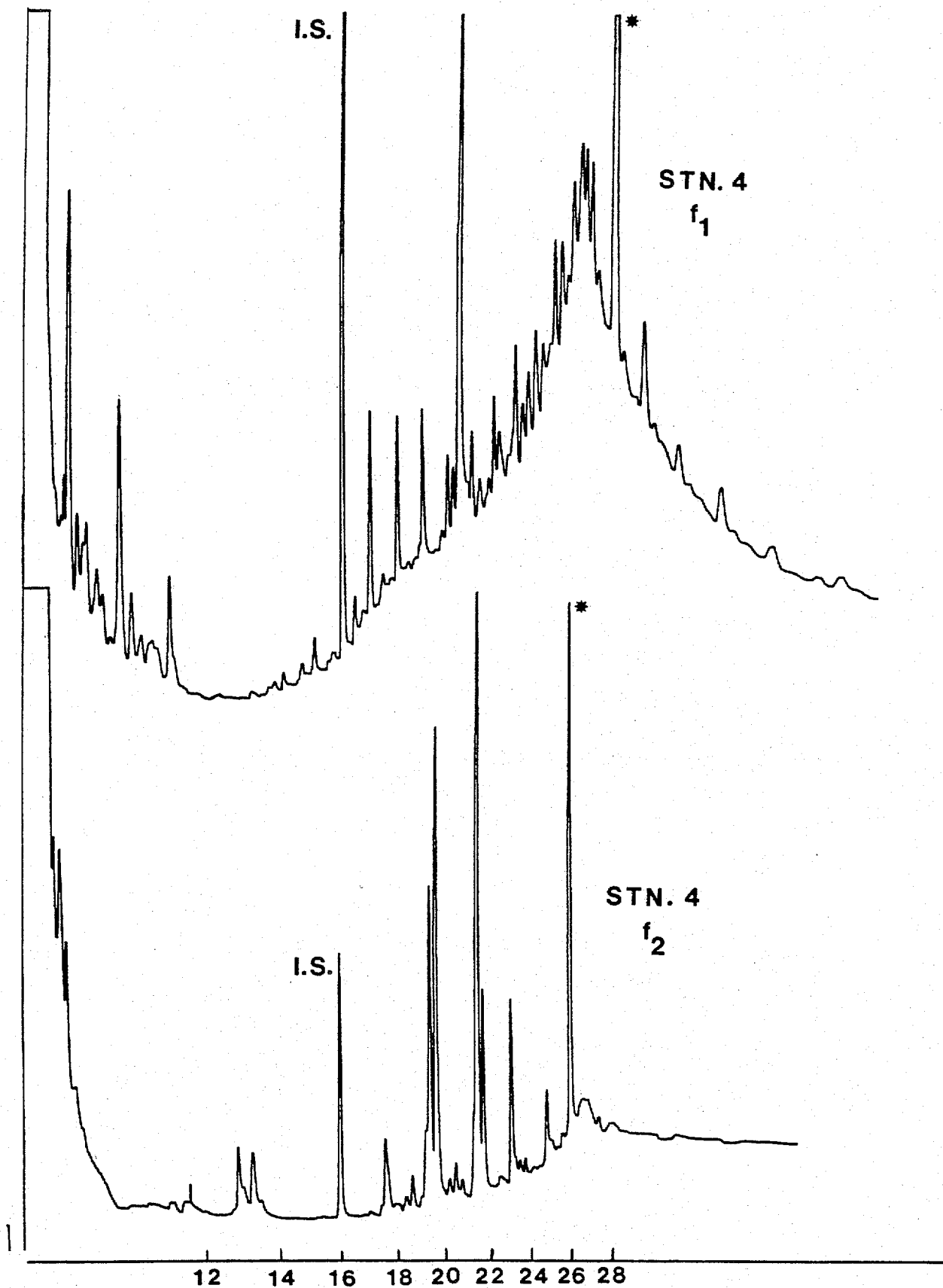
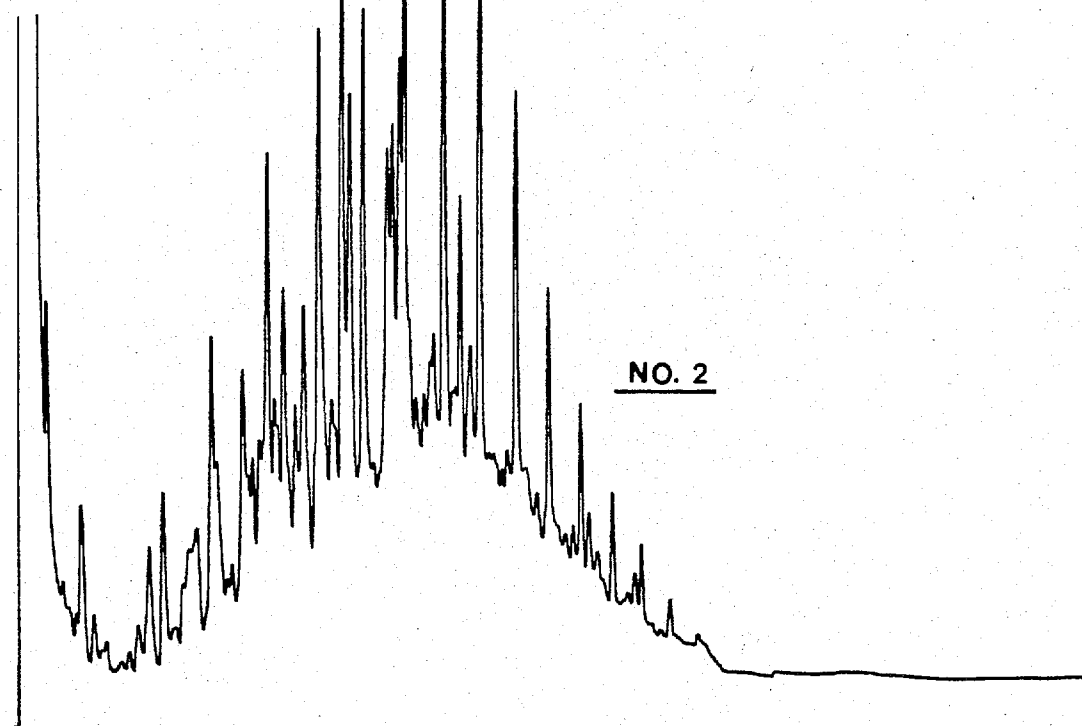
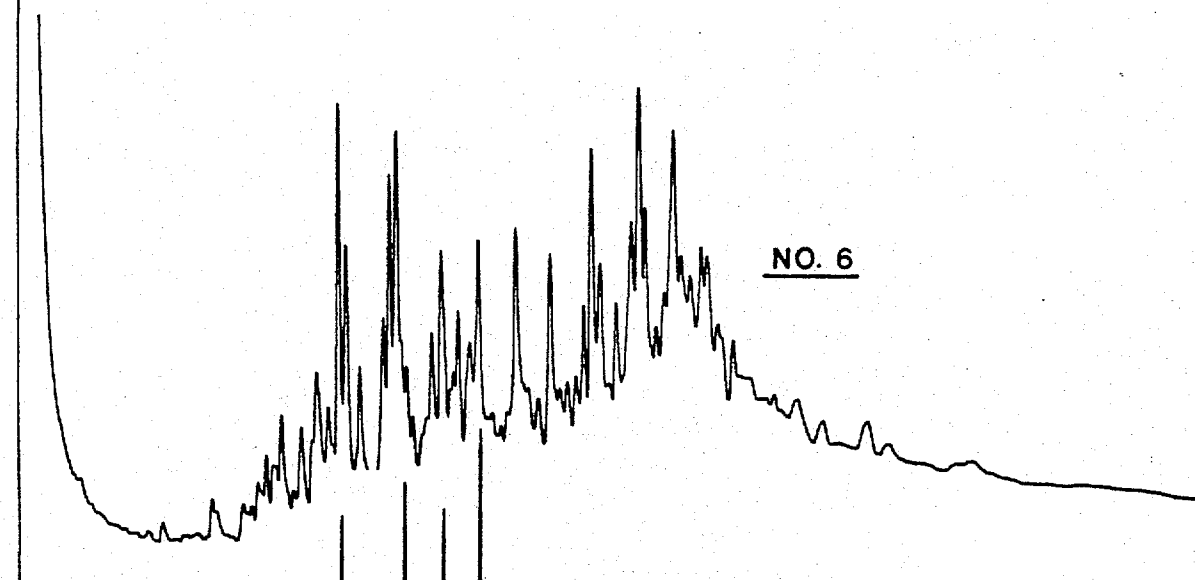
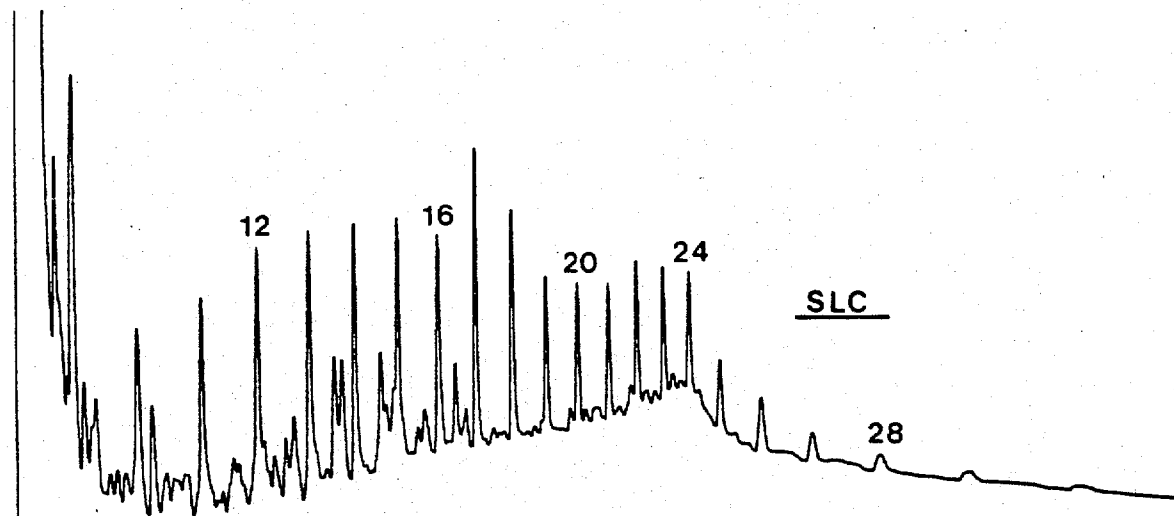


Figure 10

Chromatograms of SLC, No. 6 fuel, and No. 2 fuel. Positions of some n-alkanes are indicated on the SLC pattern.



Sample chromatograms may be compared with GC patterns of SLC and two fuel oils, No. 2 and No. 6 (Venezuelan Bunker C) (Fig. 10). The hydrocarbons in surface water have a distribution near the high end of the boiling range for the standard oils. Some of the factors that may contribute to the presence of these heavy hydrocarbons in the two estuaries are:

1. Discharge of heavy fuel oils (e.g. No. 6) and lubricating oils.

Lubricating oils typically show a large, featureless UCM consisting of high-boiling material (4). Recently the South Carolina Department of Health and Environmental Control (DHEC) conducted a water quality survey of marinas in Beaufort County (5). Individual 4-6 ring PAH were measured in the sediments, with higher concentrations nearer the marinas.

2. Accumulation of the higher molecular weight components of light fuel oils as the volatiles evaporate.

3. Input of oil residues and combustion hydrocarbons through urban runoff and atmospheric deposition. PAH and other hydrocarbons emitted by automobiles and other combustion sources can enter estuaries directly by aerial fallout, or indirectly by being deposited onto city streets and washed off by storm drainage. Recently Hoffman *et al.* (6) estimated inputs of 665 metric tons total hydrocarbons and 0.7 metric tons PAH to Narragansett Bay, RI through urban runoff. Most of the PAH were 3-ring and higher. Wade (7) collected 120 rain plus dry deposition samples at four stations around the lower Chesapeake Bay. The atmospherically derived hydrocarbons showed a pronounced UCM, centering around C₂₇ or C₂₉.

Comparison of FS and GC for Petroleum Analysis

The fluorescence of crude and refined petroleum products is mainly due to the presence of PAH, and a major drawback of FS analysis is that the aromatic content of different oils varies substantially. Several crudes, fuel oils, and used crankcase oil gave fluorescence responses differing 60-fold when measured at the wavelengths used for SLC equivalents analysis (320 nm EX, 380 nm EM) (Table 5). It is widely recognized that FS gives only an estimate of hydrocarbon pollution, and one objective of this project was to determine whether FS and GC results could be correlated.

Hydrocarbon concentrations in Charleston Harbor samples measured by FS and GC are compared in Table 6, and data from the harbor and Winyah Bay (1) are plotted in Fig. 11. Although the regressions are significant ($p < 0.01$) the data are scattered and the correlations are weak ($r^2 = 0.42 - 0.65$) (Table 7). The 95% confidence interval has been constructed for the combined data from both estuaries (Fig. 11). This interval for an individual FS value predicted from a GC measurement is a factor of 5-6 in the 0.5-10 $\mu\text{g/L}$ range. Thus a sample containing 1.0 $\mu\text{g/L}$ hydrocarbons by GC could be expected in 95% of the cases to show 0.24-6.5 $\mu\text{g/L}$ SLC equivalents by FS, with an average of 1.3 $\mu\text{g/L}$.

Comparison of Petroleum Levels in Charleston Harbor and Winyah Bay

Charleston is a much more heavily used estuary than Winyah Bay, so it is not surprising that its surface water is more polluted with hydrocarbons. Oil concentrations in the harbor varied by more than an order of magnitude (Table 3) and averaged between 2-6 $\mu\text{g/L}$ (SLC equivalents) in 3 open-channel sampling areas (Table 8). The only spot in Winyah Bay containing comparable oil levels was the turning basin of the Sampit River, where an average of 3.0 $\mu\text{g/L}$ SLC equivalents was found. At other points in the bay, petroleum residues were $< 1.0/\text{L}$ (Table 8).

Table 5. Relative Fluorescence of Crude and
Refined Oils at 320 nm EX and 380 nm EM.

<u>Oil</u>	<u>Relative Fluorescence</u>
No.2 fuel	0.068
Automobile lubricating oil ^a	0.10
Used crankcase oil	0.10
Kuwait crude oil	0.73
South Louisiana crude oil	1.00
No. 6 fuel ^b	4.1

a) Quaker State 10W-40

b) Venezuelan Bunker C

SUGGESTIONS FOR FURTHER RESEARCH

This study and the one before it (1) have provided the first baseline data for petroleum in South Carolina estuaries. Fluorescence and GC measurements indicate the presence of heavy hydrocarbons in surface waters, with higher levels in Charleston Harbor than Winyah Bay. These heavy hydrocarbons may have diverse sources, and the relative importance of urban runoff, atmospheric deposition, and discharges from ships and industries should be investigated to determine the main hydrocarbon contributors.

Hydrocarbon concentrations in the water column are transient. Because high molecular weight organic compounds are strongly adsorbed to particulate matter, they are removed from the water column by sedimentation. The sediments of an aquatic system thus serve as a long-term reservoir where pollutants are concentrated and recycled by resuspension, diffusion into overlying water, and uptake by bottom-feeding organisms. A further study of pollutants in the South Carolina estuaries should include a survey of the sediments for hydrocarbons and other pollutants, as was done in the DHEC study of marinas (5).

Although a measurement of total hydrocarbon levels is useful for monitoring purposes, a knowledge of specific aromatic hydrocarbon concentrations is more useful for assessing the toxicant burden of the estuary. Individual aromatic compounds vary widely in their toxicities; a few are highly carcinogenic (e.g. benzo[a]pyrene, benz[a]anthracene). We recommend that further investigations include the measurement of individual PAH. This would be best carried out using capillary GC or high performance liquid chromatography (HPLC), with mass spectral confirmation for selected samples.

Table 6. Comparison of FS and GC for Petroleum Analysis in Charleston Harbor

Date	Station	FS, SLC Equivalents, $\mu\text{g/L}$	GC, Total Hydrocarbons $\geq \text{C}_{12}$	GC/FS
2/19/83	1	0.82	0.49	0.60
	2	0.49	1.0	2.0
	3	0.49	1.3	2.7
	4	0.45	0.90	2.0
	6	1.0	1.4	1.4
	8	0.62	0.42	0.68
4/30/83	1	0.81, 1.9	1.3, 2.1	1.6, 1.1
	2	2.7	2.6	0.96
	6	0.61, 1.1	0.93, 1.4	1.5, 1.3
	7	5.3	3.6	0.68
	8	1.1	1.5	1.4
6/84	1	1.2	1.2	1.0
	2	2.7	2.3	0.85
	4	2.6	2.4	0.92
	6	3.2	1.6	0.50
	7	7.0	1.8	0.26
	8	2.1	1.1	0.52
2/16/84	1	3.1	0.71	0.24
	2	3.2, 7.3	1.2, 10.7	0.38, 1.5
	4	24.5	8.7	0.36
	6	18.3	5.9	0.32
	7	10.8	3.8	0.35
	8	4.5	0.73	0.16
3/2/84	1	1.7	1.1	0.65
	2	2.1, 2.6	1.4, 2.1	0.67, 0.81
	4	2.4	0.46	0.19
	6	3.0	0.80	0.27
	7	4.2	0.93	0.10
	8	1.3	0.31	0.24

Table 7. Regression Parameters for: $\log \text{HC}_{\text{FS}} = \log \text{HC}_{\text{GC}} + b$

	<u>n</u>	<u>m</u>	<u>b</u>	<u>r</u> ²	Standard error of <u>regression</u> ^a
Charleston Harbor	33	0.82	0.21	0.43	0.34
Winyah Bay	17	0.75	-0.17	0.65	0.25
Combined sets	50	0.80	0.084	0.42	0.36

a) $s_{y \cdot x} = (\text{SS}_{\text{residuals}}/n-2)^{\frac{1}{2}}$

Table 8. Comparison of Petroleum Concentrations in Charleston Harbor and Winyah Bay

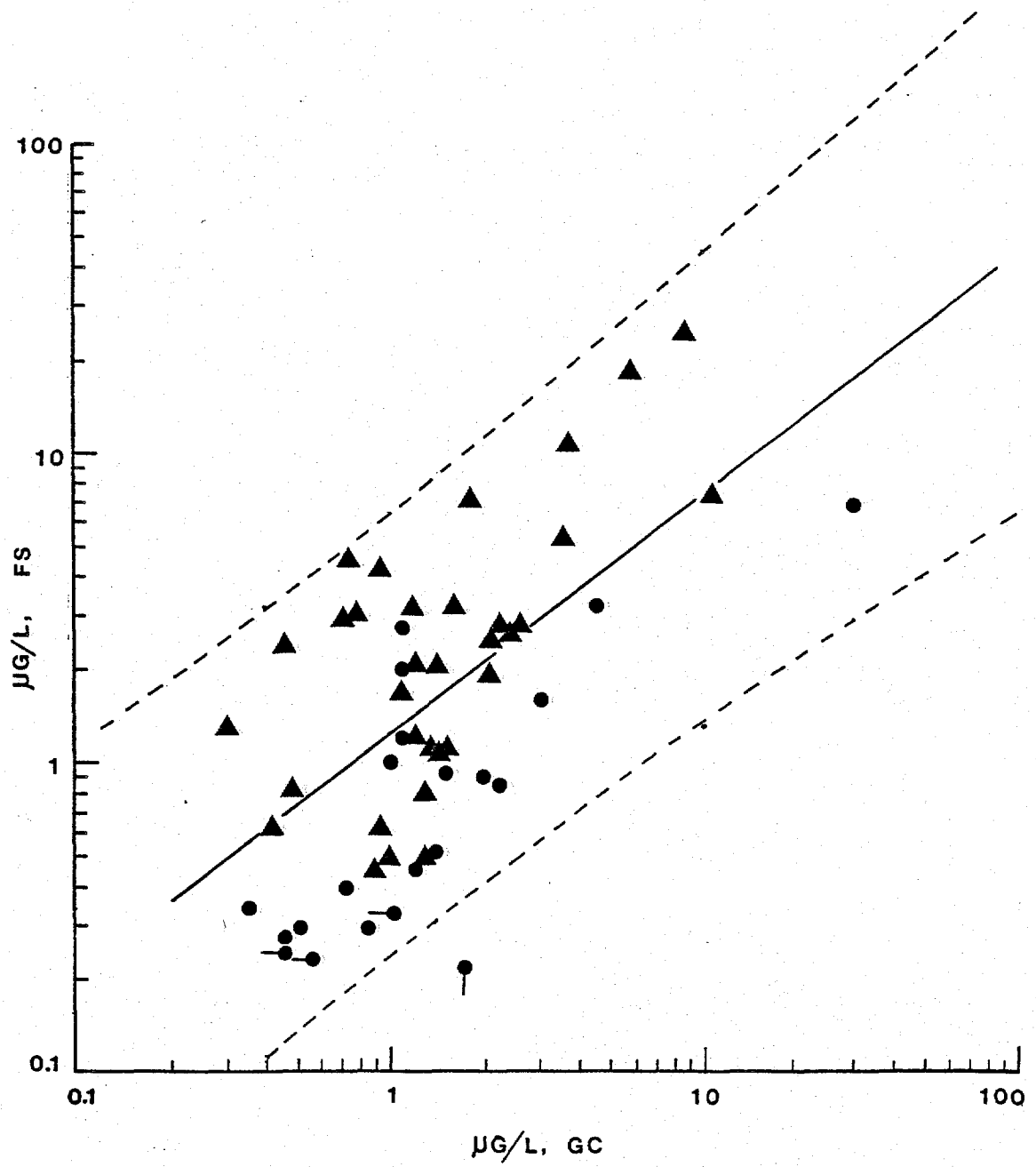
	Number of Sampling Dates	Hydrocarbons, $\mu\text{g/L}$ (mean \pm S.D.)	
		FS ^a	GC
<u>Charleston Harbor</u>			
Cooper River (Stns. 1&2)	5	2.1 \pm 1.4	2.2 \pm 2.9
Charleston Harbor Battery & Drum Island (Stns. 4&6)	5	5.8 \pm 8.4	3.0 \pm 2.9
Charleston Harbor- Ft. Johnson (Stn. 8)	5	1.9 \pm 1.5	0.81 \pm 0.49
<u>Winyah Bay</u>			
Upper Sampit River	9	0.75 \pm 0.78	<0.78 \pm 0.32
Sampit R. Turning Basin	9	3.0 \pm 2.6	4.2 \pm 8.2
Upper Winyah Bay	9	0.61 \pm 0.62	<0.98 \pm 0.46
Lower Winyah Bay	2	<0.38 \pm 0.25	<0.68 \pm 0.45

a) SLC equivalents

Figure 11

FS vs. GC analysis for hydrocarbons in surface water, after alumina cleanup and saponification. Solid = regression line, dotted = 95% confidence interval for single predicted FS from measured GC.

- Winyah Bay
- ▲ Charleston Harbor
- below detection limit by GC
- below detection limit by FS



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